

THE RELATION BETWEEN SOIL ACIDIFICATION AND ELEMENT CYCLING

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Abstract. Controversy about the contribution of acidic deposition to soil acidification partly arises from different concepts of soil acidification. Differentiating between actual and potential soil acidification has proved to be appropriate for properly identifying and quantifying the natural and anthropogenic sources of protons. Actual soil acidification is primarily manifested by leaching of cations from the soil, regulated by the mobility of major anions. Leaching of HCO_3^- and RCOO^- occurs naturally whereas leaching of NO_3^- and SO_4^{2-} is mainly caused by land use in agricultural soils and by acidic deposition in forest soils. Potential soil acidification is primarily due to accumulation of atmospherically derived N and S. This potential acid threat is partly realized by mineralization processes after the removal of vegetation.

1. Introduction

In recent decades, concern has grown about the potential impact of acid rain on land and water. The adverse effects of acid rain on surface water chemistry and biota in fresh water are recognized as a major environmental problem over vast regions of Europe and North America (Baker and Schofield, 1982; Driscoll *et al.*, 1980; Hall *et al.*, 1984). Furthermore, soil acidification induced by acid rain may play a key role in the forest dieback in Western Europe (Ulrich *et al.*, 1979; Ulrich and Matzner, 1983).

Until now, the relative importance of acid rain in soil acidification has been a matter of controversy in the literature. Some authors believe that the contribution of acid rain to soil acidification in Western Europe and America is minimal compared with natural causes and land use (Rosenqvist *et al.*, 1980; Krug and Frink, 1983), whereas others state the opposite (Ulrich and Matzner, 1983; Driscoll and Likens, 1982; Van Breemen *et al.*, 1984a, b).

This dissension is mainly due to different concepts of soil acidification. This is, amongst others, shown by the recent discussion between Krug (1985) and Van Breemen *et al.* (1985) on the relevance of H^+ budgets. According to Krug, H^+ budgets as presented by Van Breemen *et al.* (1984a, b) should not be used to estimate soil acidification rates, since these budgets only account for net H^+ transformations, thus excluding the acidification induced by the accumulation of acid organic matter. This controversy shows that an unambiguous concept of soil acidification is a prerequisite in assessing the contribution of natural and anthropogenic H^+ sources to soil acidification.

In this paper we give an overview of the concepts of soil acidification in literature and redefine the concept of Van Breemen *et al.* (1984a, b) by distinguishing actual and

potential soil acidification. To promote the standardization of the concept and measurement of soil acidification we further present an overview of:

- (i) The relation between actual and potential soil acidification by various proton sources and the cycles of major elements: C, N, S, and cations.
- (ii) Methods for measuring actual and potential soil acidification.

2. Concepts of Soil Acidification

The pH is generally used to indicate the acidity of the soil and it governs many ecologically important reactions. However, production of H^+ in the soil, if any, is only partially reflected in changes of the pH. For this reason, Van Breemen *et al.* (1984a, b) define soil acidification in terms of a capacity factor rather than an intensity factor, such as the pH. Analogous to aqueous systems, they define soil acidification as a decrease in the acid-neutralizing capacity (ANC) of the inorganic fraction of the soil including the solution phase. ANC is defined as the sum of the basic components minus the strongly acidic components:

$$ANC_m = B_m - A_m, \quad (1)$$

where B – basic components (the cations that contribute depend on the reference pH chosen), A – strongly acidic components (anions of strong acids), and m – mineral soil.

Soil acidification or ANC decrease is thus only associated with the net removal (weathering) of cations and the net accumulation (precipitation) of anions in the mineral soil. The organic phase is not included 'to simplify calculations'. This leads to the statement that the transfer of cations from the mineral soil to organic matter should be considered soil acidification (Van Breemen *et al.*, 1985). However, this is highly artificial. Organic matter is an integral part of the soil and exchangeable cations on carboxyl groups also contribute to the ANC. Furthermore, accumulation of N and S in organic matter is an increase in strongly acidic components thus decreasing the ANC. This potential source of acidification can be accounted for in the same way as the accumulation of S in the inorganic phase. Both phenomena spread the impact of acidic deposition in time. Immobilization of atmospheric N and S may lead to large H^+ loads after clear felling of forests by mineralization and nitrification processes (Likens *et al.*, 1969; Vitousek *et al.*, 1979), whereas precipitation (or adsorption) of sulphate may induce H^+ production after reduction of SO_2 deposition by dissolution (or desorption) processes (Prenzel, 1983).

Consequently, soil acidification had better be defined in terms of a decrease in ANC of the total solid (mineral and organic) and solution phase of the soil. The gas phase may be considered irrelevant because of its highly dynamic composition. In order to separate actual and potential acidification we differentiate the acid-neutralizing capacity (ANC) and the base-neutralizing capacity (BNC) by defining ANC as the sum of the basic components and BNC as the sum of the acidic components of the soil:

$$ANC_s = B_m + B_o, \quad (2)$$

$$BNC_s = A_m + A_o, \quad (3)$$

where A = strongly and weakly acidic components, s = solid and solution phase (total soil), and o = organic phase.

At present, BNC has not been defined but it is simply used as the opposite of ANC (Krug, 1985; Van Breemen *et al.*, 1985).

Actual soil acidification is now defined as a decrease in ANC_s (the ANC of the total soil) and potential soil acidification as an increase in BNC_s . Thus, actual acidification is reflected by cation removal and potential acidification by anion retention.

Contrary to Van Breemen *et al.* (1984a, b), we also include the weakly acidic organic acids in our definition of BNC_s . The exclusion of these components was criticized by Krug (1985). Although Krug and Frink (1983) did not define soil acidification, their approach suggests that it is mainly related to an increase in exchange acidity caused by the accumulation of acid organic matter. This increases the BNC of the soil, as we defined it, and should thus be considered potential soil acidification. This potential load will partly be realized by dissociation of H^+ when the pH of acid forest soils is raised by liming. However, under ambient conditions this increase in BNC is irrelevant to the actual soil acidification as indicated by Van Breemen *et al.* (1985).

3. Processes Affecting the Hydrogen-Ion Cycle

The H^+ cycle is the most complex of all element cycles, being affected by virtually every biochemical reaction (Sollins *et al.*, 1980; Driscoll and Likens, 1982; Van Breemen *et al.*, 1984a). Attempts to discuss H^+ -producing and H^+ -consuming processes in soil frequently become bogged down in details about isolated biochemical processes, such as bioproduction and dissociation of CO_2 or nitrification, which contribute little to the understanding of soil acidification in an ecosystem. Furthermore, these processes are often considered to be the main cause of natural soil acidification (Bache, 1980; Holowaychuk and Lindsay, 1982; Isermann, 1983), thus concealing the ultimate driving force for this phenomenon.

As a general rule, it can be stated that soil acidification is caused by the uncoupling of element cycles in an ecosystem (Ulrich, 1983; Matzner and Ulrich, 1983). Consequently, it is vitally important to synthesize information about all relevant processes in element cycling in relation to H^+ cycling. The most important processes are given in Table I. This table is modified after Van Breemen *et al.* (1984a), who gave a comprehensive survey of the different H^+ transfer processes in an ecosystem and their relation to soil acidification. In this context, the terms H^+ source and H^+ sink relate respectively to acid production and acid consumption in the soil solution.

Complete budgets of the total elemental turnover in each compartment of the soil-plant system account for all these H^+ -transfer processes (Driscoll and Likens, 1982; Ulrich and Matzner, 1983; Van Breemen *et al.*, 1984a, b) and give insight in actual and potential soil-acidification rates. Incomplete budgets, for example by ignoring processes such as N turnover (Sollins *et al.*, 1980), fluxes of anions (Likens *et al.*, 1979) or plant uptake (Johnson *et al.*, 1983), may lead to erroneous conclusions with respect to the rates and causes of soil acidification. To identify and quantify natural and

TABLE I

The relation between H⁺-producing and H⁺-consuming processes in the soil (modified after Van Breemen *et al.*, 1985)

H ⁺ sources	H ⁺ sinks
Uptake of cations	Uptake of anions
Mineralization of anions	Mineralization of cations
Oxidation reactions	Reduction reactions
Dissociation of weak acids (CO ₂ , organic acids)	Association of weak acids (CO ₂ , organic acids)
Weathering, desorption of anions precipitation, adsorption of cations	Weathering, desorption of cations precipitation, adsorption of anions

anthropogenic causes of soil acidification, it is appropriate to examine the cycles of major elements in more detail as shown by Reuss (1977), who gave a brief description of the most important acidity relationships in the N and S cycle. First, the cycles relating to the major anions in soil (HCO₃⁻, RCOO⁻, NO₃⁻, and SO₄²⁻) will be reviewed, viz., the C, N and S cycles. Next, a review of the cation cycle will be given without differentiating between cations.

4. The Carbon Cycle

The main processes within the C cycle are shown in Figure 1. The reaction equations of the H⁺-transfer (and H⁺-indifferent) processes are summarized in Table II, together with those of the N, S, and cation cycles. Formation of carbohydrates through photosynthesis (pathway 1; reaction 1^A) followed by mineralization of photosynthetically formed organic matter (pathway 2a, b; reaction 1^B) or by root respiration (pathway 3) are the transport mechanisms of CO₂ from the atmosphere to the gas phase of the soil. Some of the CO₂ gas returns to the atmosphere via diffusion (pathway 4). Part of the CO₂ remaining in the soil may dissociate in water, leading to an acid production (pathway 5a, reaction 2^A).

The dissociation of CO₂ is a very dominating H⁺ source in calcareous soils of high pH. In non-calcareous soils with pH above 5, CO₂ is still an important H⁺ source. Leaching studies in non-calcareous soils of unpolluted regions indicate that carbonic acid dominates the leaching process in temperate and tropical coniferous sites (Reuss, 1977; Johnson *et al.*, 1977; Johnson and Cole, 1980; Cronan *et al.*, 1978). However, in acidic soils with a pH less than 5, the acidifying effect of CO₂ is negligible. This can be deduced from the pK value of reaction 2^B (pK = 7.81) and CO₂ pressures of 5 to 20 mbar, which are commonly occurring values in well-drained soils. Consequently, it is misleading to compare the effect of CO₂ with acid rain without making a distinction between non-acidic and acidic soils, as done by Krug and Frink (1983).

In a natural (not anthropogenically influenced) ecosystem, further acidification results from organic acids that are intermediate by-products of the decomposition of organic

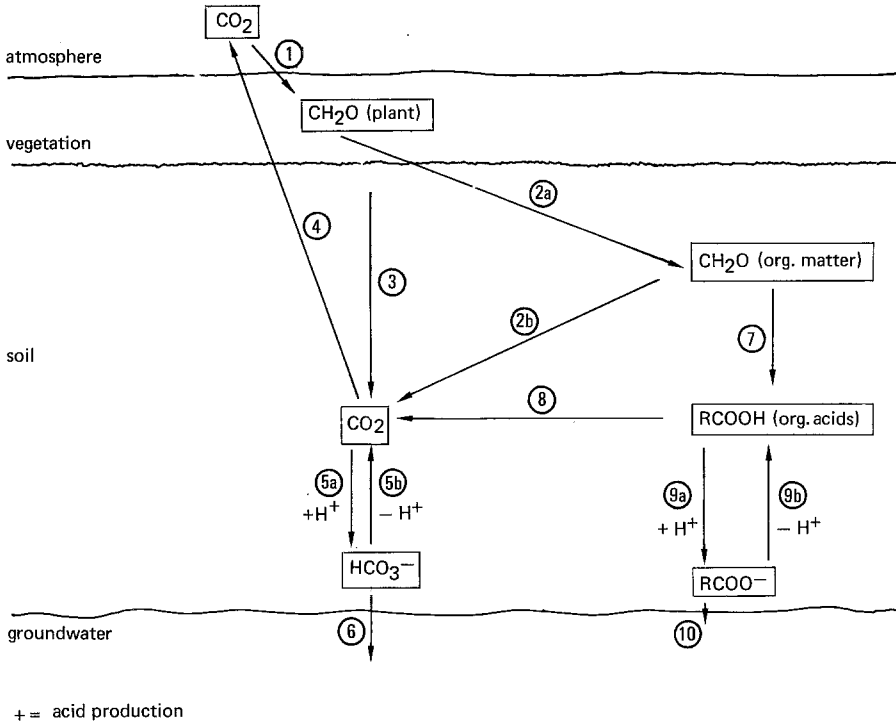


Fig. 1. Schematic presentation of the carbon cycle. 1, Photosynthesis; 2^a, Accumulation of organic C; 2^b, Mineralization of organic C; 3, Respiration; 4, Diffusion of CO_2 ; 5^a, Dissociation of CO_2 ; 5^b, Protonation of HCO_3^- ; 6, Leaching of HCO_3^- ; 7, Formation of organic acids; 8, Oxidation of organic acids; 9^a, Dissociation of organic acids; 9^b, Protonation of organic anions; 10, Leaching of organic anions.

matter to CO_2 . Especially, under unfavorable conditions such as cold, wet climates and low nutrient status, both mineralization and humification of low-molecular organic acids are inhibited (Van Breemen and Brinkman, 1976). In such situations, organic acids play an important role in soil acidification, because they can deprotonate even at low pH values (pathway 9a, reaction 5^A). Leaching studies in arctic and (sub)alpine forest soils of unpolluted regions reveal that organic anions are dominant in soil-solution chemistry (Johnson *et al.*, 1977; Ugolini *et al.*, 1977; Cronan *et al.*, 1978). The acid production resulting from dissociation of organic acids is neutralized by weathering (and desorption) of cations (especially Al and Fe) which may form a complex with the organic anions (reaction 6^A). Transport of Al and Fe as metal-organic complexes is generally accepted as an important transport mechanism of these elements in well-drained acid soils (Schnitzer and Skinner, 1963; Mokma and Buurman, 1982).

Other mechanisms that may be responsible for the transport of Al (not Fe) are transport in ionic form (Van Schuylenborgh and Bruggenwert, 1965) and transport as an inorganic alumino-silicate complex (Farmer *et al.*, 1980; Childs *et al.*, 1983). Leaching of Al and Fe rarely proceeds beyond 50 to 100 cm in well-drained soils. This process,

TABLE II
Reaction equations of H⁺-transfer processes in the C, N, S, and Cation cycles

Process from left to right	Reaction equation	Process from right to left
The C cycle		
1 ^A Photosynthesis	$\text{CO}_2 + \text{H}_2\text{O}$	respiration
2 ^A Dissociation of CO ₂	$\text{CO}_2 + \text{H}_2\text{O}$	protonation of HCO_3^-
3 Formation of formic acid	$2\text{CH}_2\text{O} + \text{O}_2$	$\text{CH}_2\text{O} + \text{O}_2$
4 Oxidation of formic acid	$2\text{HCOO}^- + \text{O}_2 + 2\text{H}^+$	$\text{HCO}_3^- + \text{H}^+$
5 ^A Dissociation of organic acids	RCOOH	$\rightarrow 2\text{HCOO}^- + 2\text{H}^+$
6 ^A Formation of an aluminium-organic complex	$3\text{RCOOH} + \text{Al}(\text{OH})_3$	$\rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$
		$\rightleftharpoons \text{RCOO}^- + \text{H}^+$
		$\rightleftharpoons (\text{RCOO})_3\text{Al} + 3\text{H}_2\text{O}$
The N cycle		
7 Fixation of N ₂	$4\text{ROH} + 2\text{N}_2 + 3\text{CH}_2\text{O}$	
8 ^A Ammonification	$\text{RNH}_2 + \text{H}_2\text{O} + \text{H}^+$	$\rightarrow 4\text{RNH}_2 + 3\text{CO}_2 + \text{H}_2\text{O}$
9 ^A Volatilization of NH ₃	NH_4^+	$\rightleftharpoons \text{ROH} + \text{NH}_4^+$
10 Nitrification	$\text{NH}_4^+ + 2\text{O}_2$	$\rightleftharpoons \text{NH}_3 + \text{H}^+$
11 Uptake of NO ₃ ⁻	$\text{ROH} + \text{NO}_3^- + \text{H}^+ + 2\text{CH}_2\text{O}$	$\rightarrow \text{RNH}_2 + 2\text{H}^+ + \text{H}_2\text{O}$
12 Denitrification	$5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+$	$\rightarrow \text{RNH}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$
13 Chemodenitrification	$\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+$	$\rightarrow 2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O}$
14 Absorption of NH ₃	$\text{ROH} + \text{NH}_3$	$\rightarrow 4\text{NO}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$
15 Absorption of NO ₂	$4\text{ROH} + 4\text{NO}_2 + 7\text{CH}_2\text{O}$	$\rightarrow \text{RNH}_2 + \text{H}_2\text{O}$
16 Oxidation of NO ₂	$4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$	$\rightarrow 4\text{RNH}_2 + 7\text{CO}_2 + 5\text{H}_2\text{O}$
		$\rightarrow 4\text{NO}_3^- + 4\text{H}^+$
		uptake of NH_4^+
		formation of NH_4^+
		protonation of organic anions
		hydrolysis of an
		aluminium-organic complex

Table II (continued)

Process from left to right	Reaction equation	Process from right to left
The S cycle		
17 Uptake of SO_4^{2-}	$\text{ROH} + \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{CH}_2\text{O}$	$\rightarrow \text{RSH} + 2\text{CO}_2 + 3\text{H}_2\text{O}$
18 Mineralization of organic S	$\text{RSH} + \text{H}_2\text{O} + 2\text{O}_2$	$\rightarrow \text{ROH} + \text{SO}_4^{2-} + 2\text{H}^+$
19 Sulphate reduction	$\text{SO}_4^{2-} + 2\text{H}^+ + 2\text{CH}_2\text{O}$	$\rightarrow \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O}$
20 Oxidation of H_2S	$\text{H}_2\text{S} + 2\text{O}_2$	$\rightarrow \text{SO}_4^{2-} + 2\text{H}^+$
21 Reduction of Fe_2O_3 and SO_4^{2-}	$2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2-} + 16\text{H}^+ + 15\text{CH}_2\text{O}$	$\rightarrow 4\text{FeS}_2 + 15\text{CO}_2 + 23\text{H}_2\text{O}$
22 Oxidation of FeS_2	$4\text{FeS}_2 + 15\text{O}_2 + 8\text{H}_2\text{O}$	$\rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_4^{2-} + 16\text{H}^+$
23 Absorption of H_2S	$\text{H}_2\text{S} + \text{ROH}$	$\rightarrow \text{RSH} + \text{H}_2\text{O}$
24 Oxidation of H_2S to SO_2	$2\text{H}_2\text{S} + 3\text{O}_2$	$\rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$
25 Absorption of SO_2	$2\text{SO}_2 + 2\text{ROH} + 3\text{CH}_2\text{O}$	$\rightarrow 2\text{RSH} + 3\text{CO}_2 + 3\text{H}_2\text{O}$
26 Oxidation of SO_2	$2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$	$\rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+$
27 ^A Adsorption of SO_4^{2-}	$(\text{OH})_2\text{ex} + \text{SO}_4^{2-} + 2\text{H}^+$	$\rightleftharpoons \text{SO}_4\text{ex} + 2\text{H}_2\text{O}$
28 ^A Precipitation of SO_4^{2-}	$\text{Al}(\text{OH})_3 + \text{SO}_4^{2-} + 2\text{H}^+$	$\rightleftharpoons \text{AlOHSO}_4 + 2\text{H}_2\text{O}$
The cation cycle		
29 ^A Uptake of M^+	$\text{RCOOH} + \text{M}^+$	$\rightleftharpoons \text{RCOOM} + \text{H}^+$
30 ^A Reverse weathering of M^+	$2\text{M}^+ + \text{H}_2\text{O}$	$\rightleftharpoons \text{M}_2\text{O} + 2\text{H}^+$
31 ^A Adsorption of M^+	$\text{M}^+ + \text{H}^+\text{ex}$	$\rightleftharpoons \text{M}^+\text{ex} + \text{H}^+$
32 Weathering and uptake of M^+	$2\text{RCOOH} + \text{M}_2\text{O}$	$\rightarrow 2\text{RCOOM} + \text{H}_2\text{O}$
33 Reduction of Fe_2O_3	$2\text{Fe}_2\text{O}_3 + \text{CH}_2\text{O} + 8\text{H}^+$	$\rightarrow 4\text{Fe}^{2+} + \text{CO}_2 + 5\text{H}_2\text{O}$
34 Oxidation of Fe^{2+}	$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}_2\text{O}$	$\rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{H}^+$
		desorption of SO_4^{2-} dissolution of jurbanite
		27 ^B 28 ^B
		Mineralization of M^+ Weathering Desorption of M^+
		29 ^B 30 ^B 31 ^B

called podzolization, leads to a characteristic bleached eluviation (albic) horizon and a dark brown illuviation (spodic) horizon.

As mentioned before, this transfer of cations from the soil mineral phase to the soil organic phase is not considered soil acidification in itself. However, the leaching of Al and Fe leads to acidification (ANC decrease) in the eluviation horizon and alkalization in the illuviation horizon. Net acidification over the complete soil profile occurs when the metal-organic complexes are leached to the groundwater.

The actual acid-production rate from dissociation of weak (carbonic and organic) acids can be quantified by balancing the input versus the output for the relevant acid-producing anions (HCO_3^- and/or RCOO^-) on an annual basis:

$$\text{H}^+ \text{ production} = (\text{HCO}_3^- + \text{RCOO}^-)_{\text{out}} - (\text{HCO}_3^- + \text{RCOO}^-)_{\text{in}} \quad (1)$$

The input of HCO_3^- and RCOO^- can be considered negligible, whereas the output of these anions can be quantified by measuring their concentration and the flux of soil water. Acidification rates obtained with these balances range from about 7 to 13 $\text{kmol ha}^{-1} \text{yr}^{-1}$ for calcareous soils. This range in decalcification (acidification) rates corresponds with the solubility of CaCO_3 assuming a generally occurring range in CO_2 pressure of 5 to 20 mbar and a precipitation surplus between 200 and 400 mm yr^{-1} (De Vries and Breeuwsma, 1986). In non-calcareous soils, acidification rates vary from 1 to 4 $\text{kmol ha}^{-1} \text{yr}^{-1}$ in soils with a $\text{pH} > 5$ (Johnson *et al.*, 1977; Cronan *et al.*, 1978) to 0.1 to 0.7 $\text{kmol ha}^{-1} \text{yr}^{-1}$ for acid podzolic soils (Ulrich and Matzner, 1983; Van Breemen *et al.*, 1984b).

Decalcification and/or podzolization rates can also be calculated using a historical approach by comparing the amount of weatherable cations (ANC) in the topsoil with the amount in the presumed parent material and estimating the time since the process started. Values thus obtained for calcareous and podzolic soils in The Netherlands are in the same range as those obtained by input-output balances of HCO_3^- and RCOO^- (De Vries and Breeuwsma, 1986).

The potential acid production by weak acids can be quantified by measuring the exchange acidity by titration. However, this does not give any information on actual H^+ production resulting from dissociation. Consequently, it is wrong to assess the impact of acidic deposition compared to natural soil-forming processes by comparing the amount of H^+ in rain with the exchange acidity as done by Krug and Frink (1983). Moreover, the amount of H^+ in rain is only a small proportion of the total acid load (in The Netherlands ca. 5% because of the extremely large input of ammonium; Van Breemen *et al.*, 1982).

Air pollution may have several effects on the C cycle and thus on H^+ production. First of all, an increased acidification due to deposition and oxidation of SO_2 , NO_x , and NH_3 may decrease C mineralization (Tamm *et al.*, 1980; Popovic, 1984) and through that the natural rate of acidification, although significant effects have not always been found (Roberts *et al.*, 1980). Furthermore, acid-rain-induced H^+ production may decrease the dissociation of weak acids in non-calcareous soils and thereby reduce the leaching of organic ions (Krug and Frink, 1983). However, their hypothesis that

protonation of organic anions in the soil solution (pathway 9b, reaction 5^B) is an important buffering mechanism in acid soils is rather doubtful. First, the quantitative importance of this buffering process cannot be great, since the concentration of organic anions in the soil solution is low (Johnson *et al.*, 1977; Ugolini *et al.*, 1977; Cronan *et al.*, 1978). Furthermore, the agreement of values on decalcification and podzolization rates based on an actual approach (Van Breemen *et al.*, 1984b) and a historical approach (De Vries and Breeuwsma, 1986) indicate that the influence of anthropogenic activities on natural H⁺ production is small.

5. The Nitrogen Cycle

Nitrogen-transformation processes, which are extremely important in regulating the H⁺ cycle, can easily be misinterpreted. Therefore, we will focus on the net effect of N cycling on H⁺ transfer processes. The main biochemical processes in the N cycle are illustrated in Figure 2. Natural processes (pathways 1 to 8) are distinguished from processes mainly caused by acid rain (pathways 9 to 20). The distinction is somewhat artificial, because all processes do occur naturally and nearly all are influenced by acid rain. However, deposition of NH₃, NO_x, and reaction products (NH₄⁺, NO₃⁻) (pathways 9 to 20) is negligible in unpolluted regions and as such the distinction is useful.

An important conclusion that may be drawn from Figure 2 is that accumulation of N in biomass (organic matter, vegetation) is not accompanied by a net production or consumption of H⁺. The principal reason for this is that N is not originally present in the soil but stems from volatile N compounds (in unpolluted regions mainly N₂).

Neither the transformation of 'atmospheric' N to organic N in vegetation by fixation of N₂ (pathway 1, reaction 7) nor the internal transformation of N from soil organic matter to vegetation leads to a net H⁺ transfer. Mineralization of organic N to NH₄⁺ (pathway 2b, reaction 8^A) results in H⁺ consumption whereas NH₄⁺ uptake (pathway 3, reaction 8^B) leads to H⁺ release and the net balance is zero. If NH₄⁺ is nitrified (pathway 4, reaction 9) two H⁺ ions are produced leaving a net H⁺ balance of +1 but after NO₃⁻ uptake (pathway 6, reaction 10) the net balance is zero again. Statements that the H⁺ budget is affected by the form in which N is taken up are, therefore, wrong. The same is true for calculations of the H⁺ production resulting from biomass accumulation that are based on a certain NH₄⁺/NO₃⁻ ratio (Nilsson *et al.*, 1982).

Research on element cycling shows that N cycling does not generally contribute to the overall H⁺ production in forest ecosystems in relatively unpolluted areas (release is balanced by uptake: closed cycle) (Johnson *et al.*, 1977; Ugolini *et al.*, 1977; Cronan *et al.*, 1978; Bornmann *et al.*, 1977). A notable exception has to be made for N-fixing stands such as red alder, where the amount of NO₃⁻ produced exceeds biological demand. In this case, the natural rate of acidification resulting from an imbalance in the N cycle can be as high as 4 kmol ha⁻¹ yr⁻¹ (Johnson *et al.*, 1983; Van Miegroet and Cole, 1984). Furthermore, it should be noted that even if the N cycle is closed, it may have profound local effects on the acidification of soil layers, because of spatial uncoupling of the ion cycle (Ulrich, 1983).

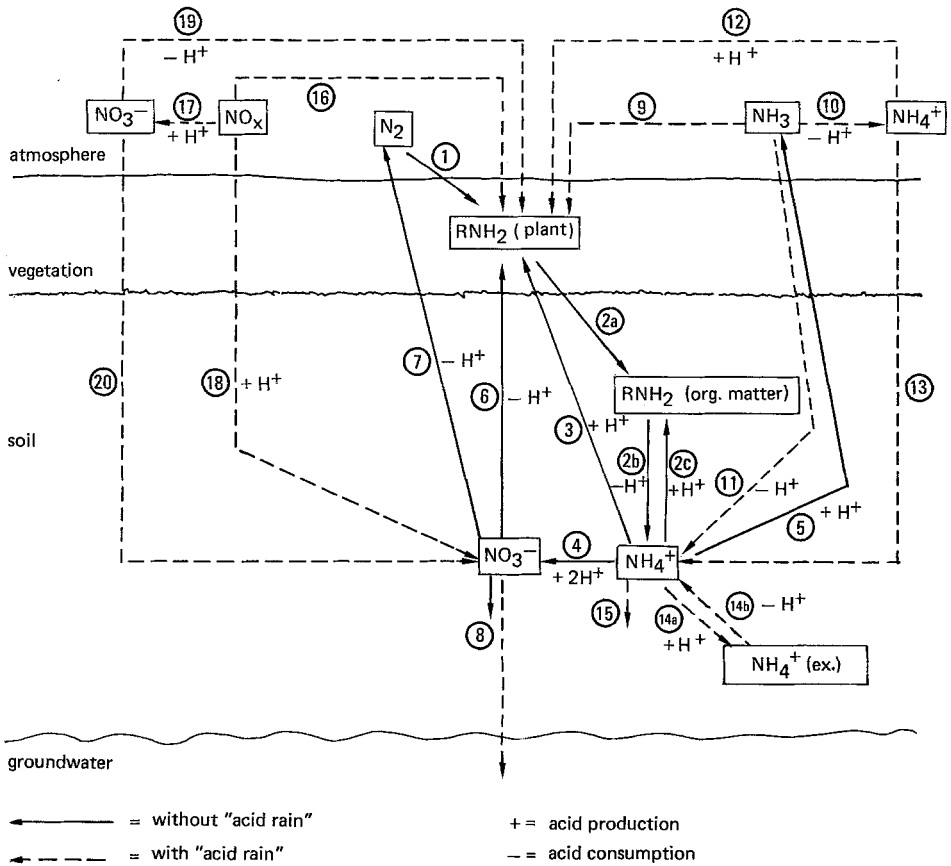


Fig. 2. Schematic presentation of the nitrogen cycle. 1, N_2 fixation; 2^a, Accumulation or organic N; 2^b, Mineralization of organic N; 2^c, N immobilization; 3, Uptake of NH_4^+ ; 4, Nitrification; 5, Volatilization of NH_3 ; 6, Uptake of NO_3^- ; 7, Denitrification; 8, Leaching of NO_3^- ; 9, Absorption of NH_3 ; 10, Protonation of NH_3 ; 11, Deposition and protonation of NH_3 ; 12, Absorption of NH_4^+ ; 13, Deposition of NH_4^+ ; 14^a, Adsorption of NH_4^+ ; 14^b, Desorption of NH_4^+ ; 15, Leaching of NH_4^+ ; 16, Absorption of NO_x ; 17, Oxidation of NO_x ; 18, Deposition and oxidation of NO_x ; 19, Absorption of NO_3^- ; 20, Desorption of NO_3^- .

When the natural cycling of N is disturbed by removal of vegetation, N reactions may become extremely important in the H^+ cycle (Likens *et al.*, 1969; Vitousek *et al.*, 1979). In this case, mineralization and nitrification of organic N to NO_3^- are not balanced by uptake of NO_3^- . Generally, it is assumed that nitrification is inhibited in acid forest soils (Campbell and Lees, 1967; Keeney, 1980). This is true in forest soils that have N deficiency (e.g., many young soils), where NH_4^+ released during decomposition of organic matter is readily taken up. However, leaching studies in several acid forest soils with ample N supply indicate that NH_4^+ may be nitrified even at low pH values (Likens *et al.*, 1969; Johnson *et al.*, 1979; Van Breemen *et al.*, 1984a, b). It has, therefore, been

suggested that availability of NH_4^+ is a major regulator for nitrification (Johnson *et al.*, 1979; Johnson and Cole, 1980). Acidification by removal of vegetation is manifested by the leaching of NO_3^- (pathway 8) with accompanying cations. In forest soils this effect is usually not important because vegetation generally regrows rapidly and clearing is not frequent. However, mineralization of N is the major source for soil acidification if biomass is removed each year, as in agricultural soils. Acidification by mineralization may also occur after a change in moisture regime from wet to dry by lowering the water-table. This effect may continue for a long time.

The N cycle can also be strongly influenced by man through (potentially) acid rain. Deposition of NH_3 has a profound effect on the N cycle in areas with intensive animal husbandry, whereas NO_x is an important pollutant in areas with heavy traffic. As stated before, there is no net H^+ transfer as long as the N compounds from the atmosphere (NH_3 , NO_x , N_2) are taken up by the vegetation, irrespective of the pathway and the medium (air or soil). The only important thing to know is the form (NH_4^+ or NO_3^-) which N enters and leaves the soil. The actual acid-production rate resulting from N transformations can thus be quantified by balancing the input of NH_4^+ (H^+ source) and NO_3^- (H^+ sink) versus the output on an annual basis (Van Breemen *et al.*, 1984a):

$$\text{H}^+ \text{ production} = (\text{NH}_4^+_{\text{in}} - \text{NH}_4^+_{\text{out}}) - (\text{NO}_3^-_{\text{in}} - \text{NO}_3^-_{\text{out}}) \quad (2)$$

where in = above forest canopy and out = below root zone.

Equation (2) represents the H^+ production resulting from removal of NH_4^+ (by uptake, nitrification or volatilization) and the H^+ consumption resulting from removal of NO_3^- (by uptake or denitrification).

The input of the N compounds can best be estimated by measuring wet deposition above the forest canopy or in a nearby open field. Although throughfall measurements give an indication of total (wet and dry) deposition of NH_3 and NO_x , this is always inaccurate because of interaction of the compounds with the canopy. However, for the assessment of an H^+ budget it is not necessary to measure dry deposition of NO_x and NH_3 , since the effect of this phenomenon on H^+ production shows up as an additional leaching of NO_3^- . Consequently, the actual acid production resulting from gaseous inputs of NH_3 and NO_x is implicitly accounted for in Equation (2) by the output of NO_3^- .

The 'immobilization' of N in organic matter forms a potential source of acidification that can be estimated from the increase in organic N in the soil over a long time period (decades). In theory, it is also possible to measure total deposition by throughfall and to calculate accumulation of organic N by subtracting uptake and output. However, this is only reasonable if denitrification can be ignored.

6. The Sulphur Cycle

Numerous authors have studied S cycling in forest ecosystems (Shriner and Henderson, 1978; Sollins *et al.*, 1980; Turner *et al.*, 1980; Meiwes and Khanna, 1981; David *et al.*,

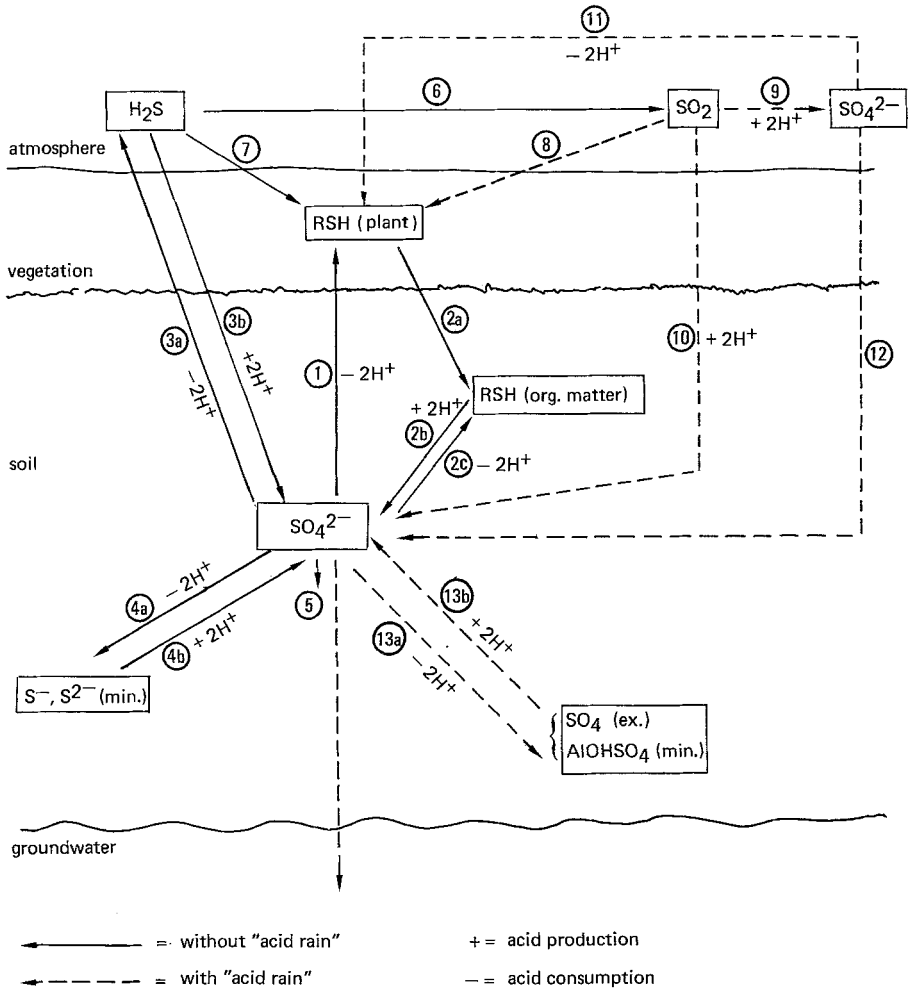


Fig. 3. Schematic presentation of the sulphur cycle. 1, Uptake of SO_4^{2-} ; 2^a, Accumulation of organic S; 2^b, Mineralization of organic S; 2^c, Incorporation of SO_4^{2-} in organic S; 3^a, Reduction of SO_4^{2-} to H_2S ; 3^b, Oxidation of H_2S to SO_4^{2-} ; 4^a, Reduction of SO_4^{2-} to FeS, FeS_2 ; 4^b, Oxidation of FeS, FeS_2 to SO_4^{2-} ; 5, Leaching of SO_4^{2-} ; 6, Oxidation of H_2S to SO_2 ; 7, Absorbion of H_2S ; 8, Absorption of SO_2 ; 9, Oxidation of SO_2 ; 10, Deposition and oxidation of SO_2 ; 11, Absorption of SO_4^{2-} ; 12, Deposition of SO_4^{2-} ; 13^a, Adsorption (precipitation) of SO_4^{2-} ; 13^b, Desorption (dissolution) of SO_4^{2-} .

1982). The major biochemical processes in the S cycle are illustrated in Figure 3. Similar to the N cycle, a distinction is made between naturally occurring processes (pathways 1 to 7) and processes mainly induced by acid rain (pathways 8 to 13).

As with N, research on element cycling in relatively unpolluted areas shows that S cycling hardly contributes to the H^+ production in a forest ecosystem (Johnson *et al.*, 1977; Ugolini *et al.*, 1977; Cronan *et al.*, 1978). In this situation, the cycle is generally closed and thus the release of sulphate by mineralization and oxidation (pathway 2b, reaction 18) resulting in H^+ production is balanced by sulphate uptake (pathway 1,

reaction 17). A notable exception are tidal flats or seabottom sediments where conveyance of sulphate by seawater and reduction to iron sulphides (pathway 4a, reaction 21) leads to a large accumulation of S, thus increasing the BNC. This potential acid load is realized after drainage by oxidation of FeS or FeS₂ to SO₄²⁻ (pathway 4b, reaction 22) leading to extremely acid sulphate soils (Van Breemen, 1975). This is, however, only of regional importance.

Uncoupling of the S cycle leads to effects that are comparable to that of N, viz., soil acidification by leaching of SO₄²⁻ (pathway 5) with accompanying cations. Contrary to N, S is originally present in most soils. Therefore, incorporation of S in vegetation could be accompanied by removal of S from the soil. However, especially in areas with SO₂ pollution, S in forest vegetation most likely stems from volatile S compounds in the atmosphere. The atmosphere always contains a certain amount of SO₂, but in industrialized countries this is relatively small compared to anthropogenically derived SO₂. Analogous to N, there is no net H⁺ transfer as long as SO₂ is taken up by the vegetation, irrespective of the pathway and the medium. However, the uptake of S by vegetation is considerably lower than that of N. The acidifying effect of SO₂, therefore, is usually high compared with that of NH₃ and NO_x (Van Breemen *et al.*, 1984a, b).

Another important difference between sulphate and nitrate is that, contrary to that of nitrate, the mobility of sulphate can be affected by soil adsorption or by precipitation (pathway 13a). Adsorption of SO₄²⁻ on sesquioxides (reaction 27^A), can be an important buffering mechanism in podzolic soils with a sesquioxide-rich B horizon (Johnson and Cole, 1977, 1980; Johnson *et al.*, 1979; Singh, 1980; Singh *et al.*, 1980; Abrahamson and Stuanes, 1980; Farrel *et al.*, 1984). Precipitation of SO₄²⁻ may occur as jurbanite (AlOHSO₄) (reaction 28^A) (Van Breemen, 1975; Nordstrom, 1982; Prenzel, 1983; Weaver *et al.*, 1985) or other basic aluminium sulphates (Singh and Brydon, 1969; Adams and Rawajfih, 1977; Nilsson and Bergkvist, 1983).

The actual H⁺ production rate caused by S transformations can be quantified by balancing the input of SO₄²⁻ versus the output on an annual basis:

$$H^+ \text{ production} = -(\text{SO}_4^{2-}{}_{\text{in}} - \text{SO}_4^{2-}{}_{\text{out}}) \quad (3)$$

where in = above forest canopy and out = below root zone.

Analogous to N, dry deposition of SO₂ followed by oxidation to SO₄²⁻ shows up as an additional leaching of SO₄²⁻, unless this compound is either taken up, or reduced, or retained via immobilization, precipitation or adsorption. In the case of S retention, the BNC of the soil increases (potential acidification). This potential acidification rate can be obtained as described for N.

7. The Cation Cycle

The relevant naturally occurring processes in the cation cycle (pathways 1 to 4), including anthropogenic influences (pathways 5 to 6) are illustrated in Figure 4. The cation cycle is strongly correlated with the cycles of C, N, and S, since the mobilities of the anions HCO₃⁻, RCOO⁻, NO₃⁻, and SO₄²⁻ regulate the leaching of cations

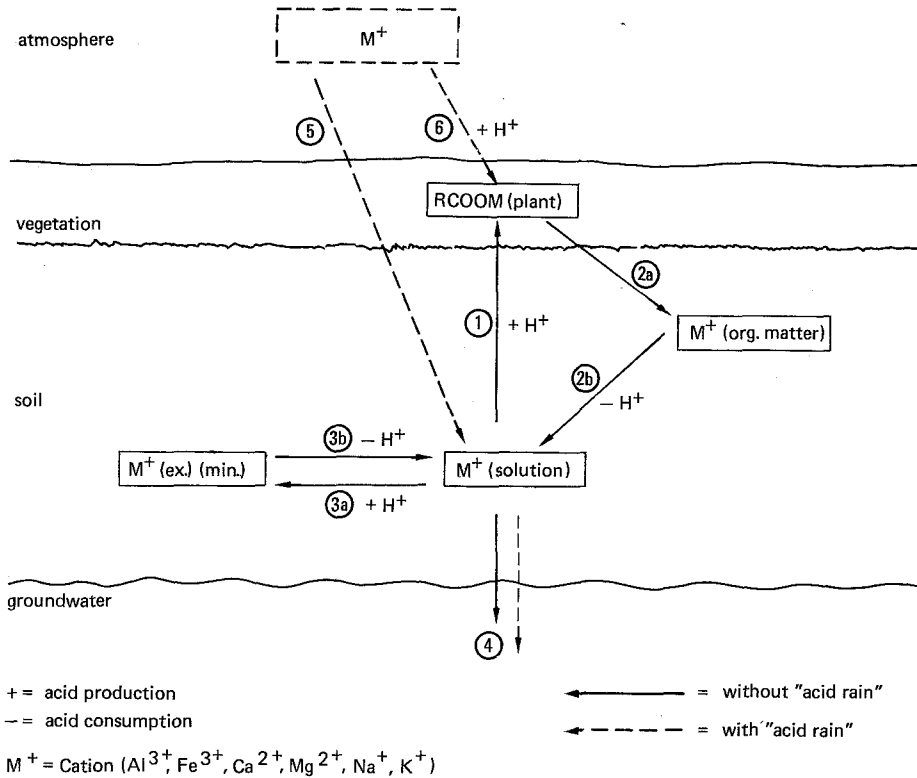


Fig. 4. Schematic presentation of the cation cycle. 1, Uptake of M^+ ; 2^a, Accumulation of M^+ in organic matter; 2^b, Mineralization of M^+ ; 3^a, Adsorption (precipitation) of M^+ ; 3^b, Desorption (dissolution) of M^+ ; 4, Leaching of M^+ ; 5, Deposition of M^+ ; 6, Absorption of M^+ .

(Johnson and Cole, 1980). In terms of an H^+ budget, mineralization (pathway 2b, reaction 29^B), weathering (pathway 3b, reaction 30^B) and desorption of cations (pathway 3b, reaction 31^B) neutralizes the acid production induced by the production of anions in mineralization and oxidation processes. Removal of cations, decreasing ANC_s , thus reflects the acid production in the soil.

The cation cycle is not completely balanced, not even in a natural forest ecosystem, since cations are leached (pathway 4) with bicarbonate and/or organic anions (natural acidification). Natural leaching of cations also occurs in periodically reduced soils such as ferrolyzed soils (reactions 33 and 34) (Brinkman, 1970). However, this process is of regional importance only.

When the natural cycling of cations is disturbed by removal of vegetation, release of cations is temporarily unbalanced by uptake. This leads to a decrease in ANC_s equal to the amount of mineralized cations. Furthermore, cations in vegetation are also removed permanently from the soil (no recycling), thus inducing a continuous decrease in ANC_s .

The acid consumption rate resulting from weathering and desorption of cations can be quantified by balancing input of cations in rain (pathways 5 and 6) against output and correcting for net cation uptake (uptake minus litterfall) on an annual basis:

$$H^+ \text{ consumption} = M_{\text{out}}^+ - M_{\text{in}}^+ + M_{\text{uptake}}^+ \quad (4)$$

where in = above forest canopy and out = below root zone.

8. Synthesis of the Element Cycles

A synthesis of all major element cycles leads to the general conclusions that actual rates of natural and anthropogenic soil acidification can be identified by the anion that is leached from the soil profile. Conjugated bases of weak acids (HCO_3^- , RCOO^-) are an indication of natural soil acidification, whereas conjugated bases of strong acids (NO_3^- , SO_4^{2-}) are indicative of anthropogenic soil acidification.

More specifically, the following conclusions may be drawn about natural and anthropogenic soil acidification, especially land use and acid rain.

8.1. NATURAL SOIL ACIDIFICATION

A net acid production in a natural ecosystem mostly results from dissociation of weak acids. The prerequisites for natural decalcification and podzolization are the presence of CO_2 in the atmosphere and the precipitation surplus. The actual acidification rate that is manifested by the leaching of HCO_3^- and/or RCOO^- with cations, can be quantified by measuring the output of these anions, since the input may be ignored.

Acidification rates thus obtained vary between 7 to 13 $\text{kmol ha}^{-1} \text{yr}^{-1}$ for calcareous soils and 0.1 to 0.7 $\text{kmol ha}^{-1} \text{yr}^{-1}$ in podzolic soils (Johnson *et al.*, 1977; Cronan *et al.*, 1978; Ulrich and Matzner, 1983; Breemen *et al.*, 1984a, b). Additional H^+ sources may be present in soils with a N-fixing vegetation and in special soils, such as acid sulphate soils and ferrolyzed soils.

8.2. REMOVAL OF VEGETATION

Removal of vegetation causes soil acidification because it leads to a continuous removal of cations from the soil. In this context, the term cation stands for all cation nutrients except NH_4^+ , because uptake of N does not contribute to soil acidification. As all anions mainly stem from the atmosphere, the acid production caused by removal of biomass can be quantified as:

$$H^+ \text{ production} = M^+ \text{ net uptake} \quad (5)$$

The acidification rate resulting from accumulation can be estimated by measuring the growth rate and chemical composition of the vegetation. Literature values from the accumulation rates in tree stems vary between 0.3 and 0.7 $\text{kmol ha}^{-1} \text{yr}^{-1}$ (Ulrich, 1983; Nilsson *et al.*, 1982). These values are indicative of the long-term acidification induced by forestry, because production forests are always in the aggradation phase. Furthermore, removal of vegetation temporarily leads to proton production, since

mineralization is not balanced by uptake. This H^+ production can be quantified as:

$$H^+ \text{ production} = (NO_3^- + SO_4^{2-}) \text{ mineralization} . \quad (6)$$

It is the realization of a potential acid threat (increase in BNC_s) caused by the immobilization of atmospherically derived N and S.

An indication of the actual acid-production rate by mineralization can be obtained by an input-output balance for NO_3^- and SO_4^{2-} in the organic toplayer and surface horizon, but it is difficult to distinguish between the influence of mineralization and that of acid rain. Data on an H^+ budget of a deforested ecosystem in Hubbard Brook (New Hampshire) indicate the acidification rate resulting from mineralization processes is about $8 \text{ kmol ha}^{-1} \text{ yr}^{-1}$ (Van Breemen *et al.*, 1984a, b). Similar values are likely in agricultural soils (De Vries and Breeuwsma, 1986), where this effect is extremely important because the crops are harvested each year.

8.3. ATMOSPHERIC DEPOSITION

Atmospheric deposition of potential acid substances such as SO_2 , NO_x , and NH_3 (acid rain) leads to soil acidification when the oxidation of these compounds to HNO_3 and H_2SO_4 is not balanced by reduction and/or incorporation of SO_4^{2-} and NO_3^- in vegetation. The actual acidification manifests itself mainly as a leaching of NO_3^- and SO_4^{2-} with accompanying cations (in acid soils mainly Al^{3+} ; Cronan and Schofield, 1979; Johnson *et al.*, 1981; David and Driscoll, 1984; Driscoll *et al.*, 1985). An indication of the actual acid production rate caused by acid rain can be obtained from the actual H^+ load to the soil and the potential H^+ load, as estimated from an input-output balance of NH_4^+ , NO_3^- and SO_4^{2-} :

$$H^+ \text{ production} = (H_{in}^+ - H_{out}^+) + (NH_{4,in}^+ - NH_{4,out}^+) - \\ - (NO_{3,in}^- - NO_{3,out}^-) - (SO_{4,in}^{2-} - SO_{4,out}^{2-}) \quad (7)$$

where in = above the forest canopy and out = below the root zone.

The potential acidification is manifested by the accumulation of organic N and S as stated before. Data of H^+ budgets for different ecosystems in Western Europe and North America indicate actual acidification rates, which vary between 1 and $6 \text{ kmol ha}^{-1} \text{ yr}^{-1}$ (Van Breemen *et al.*, 198a, b). Comparison of the literature data shows that natural soil acidification is most important in calcareous soils, whereas land use largely determines the acidification in non-calcareous agricultural soils and acid rain that of non-calcareous forest soils.

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